11. Electroplating: GILB E 4, SHAK *4* 212–244
12. Electrolysis of water solutions: SHAK *4* 170–181, 205–209
13. Commercial voltaic cells: SHAK *4* 115, J. Chem. Educ. *67* 158 (1990)
14. Corrosion: GILB G 83, M 261

SUMMARY PROBLEM

(a) anode: $2Cr^{3+}(aq) + 7H_2O \rightarrow Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$

cathode: $2BrO_3^-(aq) + 12H^+(aq) + 10e^- \rightarrow Br_2(l) + 6H_2O$

overall: $10Cr^{3+}(aq) + 6BrO_3^-(aq) + 17H_2O \rightarrow 5CrO_7^{2-}(aq) + 3Br_2(l) + 34H^+(aq)$

(b) $Pt \mid Cr^{3+},\ Cr_2O_7^{2-} \parallel BrO_3^- \mid Br_2 \mid Pt$

(c) $E^\circ = E^\circ_{ox} + E^\circ_{red} = 0.15\ V$

(d) $E^\circ = \dfrac{-\Delta G^\circ}{nF}$; $0.15\ V = \dfrac{-\Delta G^\circ}{30(9.648 \times 10^4\ J/mol \cdot V)}$; $\Delta G^\circ = 4.3 \times 10^2\ kJ/mol$

$E^\circ = -\dfrac{0.0257\ V}{n} \ln K$; $0.15\ V = \dfrac{0.0257\ V}{30} \ln K$; $K = 1.1 \times 10^{76}$

(e) $E = E^\circ - \dfrac{0.0257}{n} \ln \dfrac{[Cr_2O_7^{2-}]^5[H^+]^{34}}{[Cr^{3+}]^{10}[BrO_3^-]^6}$; $[H^+] = 10^{+0.301} = 2.00$

$E = 0.15 - \dfrac{0.0257}{30} \ln \dfrac{(0.1500)^5(2.00)^{34}}{(0.1500)^{10}(0.1500)^6} = 0.11\ V$

(f) anode: $2H_2O \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

cathode: $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$

overall: $4Cr^{3+}(aq) + 6H_2O \rightarrow 3\ O_2(g) + 4Cr(s) + 12H^+(aq)$

(g) $22.00\ g\ Cr \times \dfrac{1\ mol\ Cr}{52.00\ g\ Cr} \times \dfrac{3\ mol\ e^-}{1\ mol\ Cr} \times \dfrac{9.648 \times 10^4\ C}{1\ mol\ e^-} \times \dfrac{1\ A \cdot s}{1\ C} \times \dfrac{1}{5.4\ A} = 2.3 \times 10^4\ s \times \dfrac{1\ h}{3600\ s} = 6.3\ h$

(h) $3.75\ A \times 45\ min \times \dfrac{60\ s}{1\ min} \times \dfrac{1\ C}{1\ A \cdot s} \times \dfrac{1\ mol\ e^-}{9.648 \times 10^4\ C} \times \dfrac{1\ mol\ Cr}{3\ mol\ e^-} = 0.035\ mol\ Cr$

So, 0.035 mol Cr^{3+} converted to Cr.

Before electrolysis, mol Cr^{3+} = mol $Cr(NO_3)_3$ = 1.25 L × (0.787 mol/L) = 0.984.

After electrolysis, mol Cr^{3+} = 0.984 − 0.035 = 0.949. Then, $[Cr^{3+}] = \dfrac{0.949\ mol}{1.25\ L} = 0.759\ M$.

0.035 mol Cr plated $\times \dfrac{12\ mol\ H^+}{4\ mol\ Cr} = 0.105\ mol\ H^+$

$[H^+] = \dfrac{0.105\ mol}{1.25\ L} = 0.084\ M$; pH = 1.09

PROBLEMS

1. (a) $3\,Mg(s) + 2\,Sc^{3+}(aq) \rightarrow 3\,Mg^{2+}(aq) + 2\,Sc(s)$

   (b) $Sn(s) + Pb^{2+}(aq) \rightarrow Sn^{2+}(aq) + Pb(s)$

   (c) $6\,Cl^{-}(aq) + 2\,NO_3^{-}(aq) + 8\,H^{+}(aq) \rightarrow 3\,Cl_2(g) + 2\,NO(g) + 4\,H_2O$

3. (a) Zn anode, surrounded by Zn^{2+} ions; Cd cathode surrounded by Cd^{2+} ions. Cations move to Cd cathode, anions to Zn anode. Electrons move through the external circuit from Zn to Cd.

   (b) Cu anode, surrounded by Cu^{2+} ions; Au cathode surrounded by $AuCl_4^{-}$ ions, Cl^{-} ions. Cations move to Au cathode, anions to Cu anode. Electrons move through the external circuit from Cu to Au.

   (c) Fe anode, surrounded by OH^{-} ions, Fe^{2+}ions, $Fe(OH)_2(s)$; Cu cathode surrounded by OH^{-} ions, Cu^{2+} ions, $Cu(OH)_2\,(s)$. Cations move to Cu cathode, anions to Fe anode. Electrons move through the external circuit from Fe to Cu.

5. (a) through the external circuit (b) anode (c) Fe

7. Cations move to Cr cathode, anions to Mn anode. Electrons move through the external circuit from Mn to Cr.

$$Mn(s) \rightarrow Mn^{2+}(aq) + 2\,e^{-}$$
$$Cr^{3+}(aq) + 3\,e^{-} \rightarrow Cr(s)$$

$$3\,Mn(s) + 2\,Cr^{3+}(aq) \rightarrow 3\,Mn^{2+}(aq) + 2\,Cr(s)$$

$$Mn \mid Mn^{2+} \,||\, Cr^{3+} \mid Cr$$

9. (a) NO_3^{-} (b) S (c) MnO_2 (d) acidic solution

11. $PbSO_4 < Br^{-} < H_2S < Co < Zn$

13. Oxidizing agents: $Cr^{3+} < Sn^{2+} < Br_2$; Reducing agents: $Cr^{3+} < Hg < Sn^{2+} < H_2$

15. (a) Al^{3+} (b) Ce^{4+} (c) Al (d) Ce^{3+}

    (e) yes (f) no (g) Ce^{4+}, Hg_2^{2+}, Ag^{+} (h) Ni, Sn, Al

17. (a) Ag + I^{-}, Ni, Co (b) Ag^{+}, Hg^{2+}, NO_3^{-}, $AuCl_4^{-}$ (c) H_2S, Ag + Br^{-}, H_2, Pb

19. (a) $MnO_2 + 2e^- \rightarrow Mn^{2+}$ $E^\circ_{red} = 1.229$ V $I^- \rightarrow I_2 + 2e^-$ $E^\circ_{ox} = -0.534$ V

$E^\circ = 1.229\text{ V} + (-0.534\text{ V}) = 0.695$ V

(b) $S + 2e^- \rightarrow S^{2-}$ $E^\circ_{red} = -0.445$ V $H_2 \rightarrow H_2O + 2e^-$ $E^\circ_{ox} = 0.828$ V

$E^\circ = (-0.445\text{ V} + (0.828\text{ V}) = 0.383$ V

(c) $AuCl_4 + 3e^- \rightarrow Au$ $E^\circ_{red} = 1.001$ V $Ag \rightarrow Ag^+ + e^-$ $E^\circ_{ox} = -0.799$ V

$E^\circ = 1.001\text{ V} + (-0.799\text{ V}) = 0.202$ V

21. (a) $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^\circ_{red} = -0.828$ V

$Fe(s) + 2OH^-(aq) \rightarrow Fe(OH)_2(s) + 2e^-$ $E^\circ_{ox} = +0.891$ V

$Fe(s) + 2H_2O(l) \rightarrow Fe(OH)_2(s) + H_2$ $E^\circ = +0.063$ V

(b) $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E^\circ_{red} = 0.769$ V

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ $E^\circ_{ox} = +0.409$ V

$Fe(s) + 2Fe^{3+}(aq) \rightarrow 3Fe^{2+}(aq)$ $E^\circ = +1.178$ V

(c) $2H_2O(l) + O_2(g) + 4e^- \rightarrow 4OH^-(aq)$ $E^\circ_{red} = 0.401$ V

$Fe(OH)_2(s) + OH^-(aq) \rightarrow Fe(OH)_3(s) + e^-$ $E^\circ_{ox} = +0.547$ V

$4Fe(OH)_2(s) + O_2(g) + 2H_2O \rightarrow 4Fe(OH)_3(s)$ $E^\circ = +0.948$ V

23. (a) $E^\circ = [E^\circ_{red}\ (H^+ \rightarrow H_2) = 0\text{ V}] + [E^\circ_{ox}\ (Mn \rightarrow Mn^{2+}) = 1.182\text{ V}] = 1.182$ V

(b) $E^\circ = [E^\circ_{red}\ (Co^{3+} \rightarrow Co^{2+}) = 1.953\text{ V}] + [E^\circ_{ox}\ (Au \rightarrow AuCl_4^-) = -1.001\text{ V}] = 0.952$ V

(c) $E^\circ = [E^\circ_{red}\ (NO_3^- \rightarrow NO) = -0.140\text{ V}] + [E^\circ_{ox}\ (S^{2-} \rightarrow S) = 0.445\text{ V}] = 0.305$ V

25. If E° for $Ag^+ \rightarrow Ag = 0$ V, then all cell potentials would decrease by 0.799 V

(a) $H^+ \rightarrow H_2$ $E^\circ_{red} = 0 - 0.799 = -0.799$ V

(b) $Ca^{2+} \rightarrow Ca$ $E^\circ_{red} = -2.869 - 0.799 = -3.668$ V ; $E^\circ_{ox} = 3.668$ V

(c) $E^\circ = [E^\circ_{red}\ (NO_3^- \rightarrow NO) = -0.939\text{ V}] + [E^\circ_{ox}\ (S^{2-} \rightarrow S) = 1.244\text{ V}] = 0.305$ V ; same E°

27. (a) $E^\circ = [E^\circ_{red}\ (NO_3^- \rightarrow NO) = 0.964\text{ V}] + [E^\circ_{ox}\ (Cl^- \rightarrow Cl_2) = -1.360\text{ V}] = -0.396$ V

nonspontaneous

(b) $E^\circ = [E^\circ_{red}\ (O_2 \rightarrow H_2O) = 1.229\text{ V}] + [E^\circ_{ox}\ (Cl^- \rightarrow Cl_2) = -1.360\text{ V}] = -0.131$ V

nonspontaneous

(c) E° = [E°_{red} ($AuCl_4^- \rightarrow Au$) = 1.001 V] + [E°_{ox} ($Fe \rightarrow Fe^{2+}$) = 0.409 V] = 1.410 V

spontaneous

29. Reaction I: $4\,MnO_4^-(aq) + 12\,H^+(aq) \rightarrow 4\,Mn^{2+}(aq) + 5\,O_2(g) + 6\,H_2O$

$E^\circ = E^\circ_{red}(1) + E^\circ_{ox}(2) = 1.512\text{ V} - 1.229\text{ V} = 0.283\text{ V}$

Reaction II: $2\,Co(s) + O_2(g) + 4\,H^+(aq) \rightarrow 2\,Co^{2+}(aq) + 2\,H_2O$

$E^\circ = E^\circ_{red}(2) + E^\circ_{ox}(3) = 1.229\text{ V} + 0.282\,V = 1.511\text{ V}$

Reaction III: $5\,Co(s) + 2\,MnO_4^-(aq) + 16\,H^+(aq) \rightarrow 2\,Mn^{2+}(aq) + 5\,Co^{2+}(aq) + 8\,H_2O$

$E^\circ = E^\circ_{red}(1) + E^\circ_{ox}(3) = 1.512\text{ V} + 0.282\text{ V} = 1.794\text{ V}$

31. (a) Co^{3+} (b) O_2 (c) MnO_4^-

33. (a) no reaction; $E^\circ = -0.543$ V

(b) no reaction; $E^\circ = -0.283$ V

(c) $2\,Cr(s) + 3\,Ni^{2+}(aq) \rightarrow 2\,Cr^{3+}(aq) + 3\,Ni(s)$; $E^\circ = +0.508$ V

35. (a), (b), (c), (d)

37. (a) oxidations reductions

$Cr \rightarrow Cr^{3+} + 0.744$ V $Ni^{2+} \rightarrow Ni - 0.236$ V

$Cl^- \rightarrow Cl_2 - 1.360$ V

$2\,Cr(s) + 3\,Ni^{2+}(aq) \rightarrow 2\,Cr^{3+}(aq) + 3\,Ni(s)$; $E^\circ = 0.744\text{ V} - 0.236\text{ V} = +0.508\text{ V}$

(b) oxidations reductions

$Br^- \rightarrow Br_2 - 1.077$ V $F_2 \rightarrow F^- + 2.889$ V

$Na^+ \rightarrow Na - 2.714$ V

$F_2(g) + 2\,Br^-(aq) \rightarrow 2\,F^-(aq) + Br_2(l)$; $E^\circ = +2.889\text{ V} - 1.077\text{ V} = +1.812\text{ V}$

(c) oxidations reductions

$SO_2 \rightarrow SO_4^{2-} - 0.155$ V $Fe^{3+} \rightarrow Fe^{2+} + 0.769$ V

$NO_3^- \rightarrow NO + 0.964$ V

$2Fe^{3+}(aq) + SO_2(g) + 2\,H_2O \rightarrow 2\,Fe^{2+}(aq) + SO_4^{2-}(aq) + 4\,H^+(aq)$; $E^\circ = +0.614$ V

or

$2NO_3^-(aq) + 3\,SO_2(g) + 2\,H_2O \rightarrow 2\,NO(g) + 3\,SO_4^{2-}(aq) + 4\,H^+(aq)$; $E^\circ = +0.809$ V

39. Substitute into the formulas: $\Delta G^\circ = -nFE^\circ$; $E^\circ = \frac{0.0257}{n} \ln K$

	ΔG°	E°	K
(a)	19 kJ	-0.098 V	5×10^{-4}
(b)	-6.8 kJ	0.035 V	15
(c)	5.8 kJ	-0.030 V	0.095

41. (a) $E^\circ = \frac{-\Delta G^\circ}{nF} = \frac{-25 \times 10^3 \text{ J}}{1(9.648 \times 10^4 \text{ J/mol} \cdot \text{V})} = -0.259$ V

(b) $n = 2$ means E° is $\frac{1}{2}$ of E° obtained in (a). $E^\circ = -0.130$ V

(c) $n = 4$ means E° is $\frac{1}{4}$ of E° obtained in (a). $E^\circ = -0.0648$ V

No effect on E° but ΔG° is proportional to n.

43. $2\,MnO_4^-(aq) + 16\,H^+(aq) + 10\,e^- \rightarrow 2\,Mn^{2+}(aq) + 8\,H_2O$ $\quad E^\circ_{red} = +1.512$ V

$5\,Mn^{2+}(aq) + 10\,H_2O \rightarrow 5\,MnO_2(s) + 20\,H^+(aq) + 10\,e^-$ $\quad E^\circ_{ox} = -1.229$ V

$2\,MnO_4^-(aq) + 3\,Mn^{2+}(aq) + 2\,H_2O \rightarrow 5\,MnO_2(s) + 4\,H^+(aq)$ $\quad E^\circ = +0.283$ V

$\Delta G^\circ = -E^\circ(n)F = (-0.283 \text{ V})(10)(9.648 \times 10^4 \text{ J/mol} \cdot \text{V}) = -2.73 \times 10^5 \text{ J} = -273$ kJ

$0.283 \text{ V} = \frac{0.0257 \text{ V}}{10} (\ln K)$; $K = 8 \times 10^{47}$

45. (a) $\Delta G^\circ = (-0.695 \text{ V})(2)((9.648 \times 10^4 \text{ J/mol} \cdot \text{V})) = -1.34 \times 10^5 \text{ J} = -134$ kJ

(b) $\Delta G^\circ = (-0.383 \text{ V})(2)((9.648 \times 10^4 \text{ J/mol} \cdot \text{V})) = -7.39 \times 10^4 \text{ J} = -73.9$ kJ

(c) $\Delta G^\circ = (-0.202 \text{ V})(3)((9.648 \times 10^4 \text{ J/mol} \cdot \text{V})) = -5.85 \times 10^4 \text{ J} = -58.5$ kJ

47. (a) $\ln K = \frac{nE^\circ}{0.0257} = \frac{(2)(0.063 \text{ V})}{0.0257 \text{ V}}$; $K = 1.3 \times 10^2$

(b) $\ln K = \frac{(2)(1.178 \text{ V})}{0.0257 \text{ V}}$; $K = 6.5 \times 10^{39}$

(c) $\ln K = \frac{(4)(0.948 \text{ V})}{0.0257 \text{ V}}$; $K = 1 \times 10^{64}$

49. $Ag^+(aq) + e^- \rightarrow Ag(s)$ $\quad E^\circ_{red} = 0.799$ V

$Ag(s) + 2\,CN^-(aq) \rightarrow Ag(CN)_2^-(aq) + e^-$ $\quad E^\circ_{ox} = 0.31$ V

$Ag^+(aq) + 2\,CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$ $\quad E^\circ = 1.11$ V

$$\ln K = \frac{nE^\circ}{0.0257} = \frac{(1)(1.11\text{ V})}{0.0257\text{ V}}; \quad K = 5.8 \times 10^{18}$$

51. For the overall reaction: $Ag_2CrO_4(s) \rightleftharpoons 2\,Ag^+(aq) + CrO_4^{2-}(aq)$ $\quad K_{sp} = 1 \times 10^{-12}$

$$E^\circ = \frac{0.0257}{2} \ln (1 \times 10^{-12}) = -0.35\text{ V}$$

Half reactions: $2(Ag(s) \rightarrow Ag^+(aq) + e^-)$ $\quad E^\circ_{ox} = -0.799$ V

$Ag_2CrO_4(s) + 2e^- \rightarrow 2\,Ag(s) + CrO_4^{2-}(aq)$ $\quad E^\circ_{red} = ?$

$-0.35\text{ V} = -0.799\text{ V} + E^\circ_{red}$; $\quad E^\circ_{red} = 0.45$ V

53. (a) $E^\circ = -1.498\text{ V} + 1.763\text{ V} = +0.265$ V

(b) $$E = +0.265\text{ V} - \frac{0.0257}{6} \ln \frac{[Au^{3+}]^2}{[H_2O_2]^3[H^+]^6}$$

(c) $$E = +0.265\text{ V} - \frac{0.0257}{6} \ln \frac{(0.250)^2}{(1.50)^3(1.25)^6} = +0.288\text{ V}$$

55. (a) $E^\circ = -0.769\,V + 1.763\text{ V} = +0.994$ V

(b) $$E = +0.994\text{ V} - \frac{0.0257}{2} \ln \frac{[Fe^{3+}]^2}{[Fe^{2+}]^2[H_2O_2][H^+]^2}$$

(c) $$E = +0.994\text{ V} - \frac{0.0257}{2} \ln \frac{(0.199)^2}{(0.00813)^2(0.914)(1.32 \times 10^{-3})^2} = +0.740\text{ V}$$

57. (a) $Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$ $\quad E^\circ = 0.748$ V

$$E = E^\circ - \frac{0.0257}{2} \ln \frac{[Fe^{2+}]}{[Cu^{2+}]} = 0.748\text{ V} - \frac{0.0257}{2} \ln \frac{(0.010)}{(0.10)} = 0.778\text{ V}$$

(b) $Sn^{2+}(aq) + Co^{2+}(aq) \rightarrow Sn^{4+}(aq) + Co(s)$ $\quad E^\circ = -0.436$ V

$$E = E^\circ - \frac{0.0257}{2} \ln \frac{[Sn^{4+}]}{[Sn^{2+}][Co^{2+}]} = -0.436\text{ V} - \frac{0.0257}{2} \ln \frac{(0.010)}{(0.10)(0.10)} = -0.436\text{ V}$$

59. $E^\circ = 0.161\text{ V} + (-0.154\text{ V}) = 0.007\text{ V}$

$$E = 0.007\text{ V} - \frac{0.0257\text{ V}}{2}\ln\frac{[Sn^{4+}][Cu^{+}]^2}{[Sn^{2+}][Cu^{2+}]^2}$$

$$0 = 0.007\text{ V} - \frac{0.0257\text{ V}}{2}\ln\frac{(0.200)(0.200)^2}{(0.200)[Cu^{2+}]^2}\ ; \quad [Cu^{2+}] = 0.15\ M$$

61. $2\,Ag(s) + 2\,Br^-(aq) + 2\,H^+(aq) \rightarrow 2\,AgBr(s) + H_2(g)$

$E^\circ = 0.000\text{ V} + (-0.073\text{ V}) = -0.073\text{ V}$

$$-0.030\text{ V} = -0.0073\text{ V} - \frac{0.0257\text{ V}}{2}\ln\frac{P_{H_2}}{[Br^-]^2[H^+]^2}$$

$$-0.030\text{ V} = -0.0073\text{ V} - \frac{0.0257\text{ V}}{2}\ln\frac{1.0}{(3.73)^2[H^+]^2}\ ; \quad [H^+] = 1.4\ M$$

63. (a) $E^\circ = 1.512\text{ V} + (-1.077\text{ V}) = 0.435\text{ V}$; spontaneous

(b) $$E = 0.435\text{ V} - \frac{0.0257\text{ V}}{10}\ln\frac{[Mn^{2+}]^2}{[MnO_4^-]^2[H^+]^{16}[Br^-]^{10}}$$

$$E = 0.435\text{ V} - \frac{0.0257\text{ V}}{10}\ln\frac{(0.100)^2}{(0.100)^2(0.010)^{16}(0.100)^{10}} = 0.186\text{ V}\ ; \quad \text{spontaneous}$$

(c) $$E = 0.435\text{ V} - \frac{0.0257\text{ V}}{10}\ln\frac{(0.100)^2}{(0.100)^2(1.0\times10^{-5})^{16}(0.100)^{10}} = -0.098\text{ V}\ ; \quad \text{nonspontaneous}$$

(d) $E = 0$ V at equilibrium ; $$0\text{ V} = 0.435\text{ V} - \frac{0.0257\text{ V}}{10}\ln\frac{(0.100)^2}{(0.100)^2[H^+]^{16}(0.100)^{10}}$$

$[H^+] = 1\times10^{-4}\ M$; pH = 4.0

65. (a) $E^\circ = -0.799\text{ V} + 0.339\text{ V} = -0.460\text{ V}$

(b) $$0.060\text{ V} = -0.460\text{ V} - \frac{0.0257\text{ V}}{2}\ln\frac{[Ag^+]^2}{1.0}\ ; \quad [Ag^+] = 1.6\times10^{-9}\ M$$

(c) $K_{sp} = [Ag^+][Cl^-] = (0.10)(1.6\times10^{-9}) = 1.6\times10^{-10}$

67. (a) $Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$; $$1.000\times10^4\text{ g Al}\times\frac{1\text{ mol Al}}{26.98\text{ g Al}}\times\frac{3.00\text{ mol }e^-}{1\text{ mol Al}} = 1112\text{ mol }e^-$$

(b) $$1\text{ da}\times\frac{24\text{ h}}{1\text{ da}}\times\frac{3600\text{ s}}{1\text{ h}} = 86400\text{ s}\ ; \quad 1112\text{ mol }e^-\times\frac{9.648\times10^4\text{ C}}{1\text{ mol }e^-}\times\frac{1\text{ A}\cdot\text{s}}{1\text{ C}}\times\frac{1}{86400\text{ s}} = 1242\text{ A}$$

(c) $2\,Al_2O_3(s) \rightarrow 4\,Al(s) + 3\,O_2(g)$; $$1.000\times10^4\text{ g Al}\times\frac{1\text{ mol Al}}{26.98\text{ g Al}}\times\frac{3\text{ mol }O_2}{4\text{ mol Al}} = 278.0\text{ mol }O_2$$

69. (a) $5.0\ \text{A} \times 10.0\ \text{min} \times \dfrac{60\ \text{s}}{1\ \text{min}} \times \dfrac{1\ \text{C}}{1\ \text{A} \cdot \text{s}} = 3.0 \times 10^3\ \text{C}$

(b) $M^{3+} + 3e^- \rightarrow M$; $\quad 3.0 \times 10^3\ \text{C} \times \dfrac{1\ \text{mol}\ e^-}{9.648 \times 10^4\ \text{C}} \times \dfrac{1\ \text{mol M}}{3\ \text{mol}\ e^-} = 0.01036\ \text{mol M}$

MM = (1.19 g)/0.01036 mol = 1.1×10^2 g/mol

71. (a) 2 h + 25 min = 8700 s

$$2.00\ \text{A} \times 8700\ \text{s} \times \frac{1\ \text{C}}{1\ \text{A} \cdot \text{s}} \times \frac{1\ \text{mol}\ e^-}{9.648 \times 10^4\ \text{C}} \times \frac{1\ \text{mol Ag}}{1\ \text{mol}\ e^-} \times \frac{107.9\ \text{g Ag}}{1\ \text{mol Ag}} \times 0.82 = 16.0\ \text{g Ag}$$

(b) $16.0\ \text{g} \times \dfrac{1\ \text{cm}^3}{10.5\ \text{g}} = 1.52\ \text{cm}^3$; $\quad \text{thickness} = \dfrac{1.52\ \text{cm}^3}{6.25\ \text{cm}^2} = 0.243\ \text{cm}$

73. (a) 1 h + 22 min = 4920 s

$$6.00\ \text{A} \times 4920\ \text{s} \times \frac{1\ \text{C}}{1\ \text{A} \cdot \text{s}} \times \frac{1\ \text{mol}\ e^-}{9.648 \times 10^4\ \text{C}} \times \frac{1\ \text{mol Pb}}{2\ \text{mol}\ e^-} \times \frac{207.2\ \text{g Pb}}{1\ \text{mol Pb}} = 31.7\ \text{g Pb}$$

(b) $12.0\ \text{V} \times \dfrac{1\ \text{J}}{\text{C} \times \text{V}} \times 4920\ \text{s} \times 6.00\ \text{A} \times \dfrac{1\ \text{C}}{\text{A} \cdot \text{s}} \times \dfrac{1\ \text{kWh}}{3.600 \times 10^6\ \text{J}} = 0.0984\ \text{kWh}$

75. Calculate E° for the reaction: $\quad Pt^{2+}(aq) + 4\,Cl^-(aq) \rightarrow PtCl_4^{2-}(aq)$

$$E^\circ = \frac{0.0257\ \text{V}}{n} \ln K = \frac{0.0257\ \text{V}}{2} \ln (1 \times 10^{16}) = 0.473\ \text{V}$$

$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	$E^\circ_{\text{red}} = ?$
$Pt(s) + 4\,Cl^-(aq) \rightarrow PtCl_4^{2-}(aq) + 2e^-$	$E^\circ_{\text{ox}} = -0.73\ \text{V}$
$Pt^{2+}(aq) + 4\,Cl^-(aq) \rightarrow PtCl_4^{2-}(aq)$	$E^\circ_{\text{ox}} = 0.473\ \text{V}$

$0.473\ \text{V} = E^\circ_{\text{red}} + (-0.73\ \text{V})$; $\quad E^\circ_{\text{red}} = 1.20\ \text{V}$

77. $\text{mol } H_2 = \dfrac{(10.00\ \text{L})(0.924\ \text{atm})}{(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K})(273 + 22)\ \text{K}} = 0.382$

$$0.382\ \text{mol } H_2 \times \frac{2\ \text{mol}\ e^-}{1\ \text{mol } H_2} \times \frac{9.648 \times 10^4\ \text{C}}{1\ \text{mol}\ e^-} \times \frac{1\ \text{A} \cdot \text{s}}{1\ \text{C}} \times \frac{1}{12.0\ \text{A}} = 6143\ \text{s} = 1.71\ \text{h}$$

79. $2.00\ \text{h} \times \dfrac{3600\ \text{s}}{1\ \text{h}} \times 2.00\ \text{A} \times \dfrac{1\ \text{C}}{1\ \text{A} \cdot \text{s}} = 1.44 \times 10^4\ \text{C}$

$$\text{mol}\ e^- = 28.8\ \text{g Au} \times \frac{1\ \text{mol Au}}{197.0\ \text{g Au}} \times \frac{1\ \text{mol}\ e^-}{1\ \text{mol Au}} = 0.146$$

$$\text{Faraday constant} = \frac{\text{C}}{\text{mol}\ e^-} = \frac{1.44 \times 10^4\ \text{C}}{0.146\ \text{mol e}^-} = 9.85 \times 10^4\ \text{C}$$

81. $0.129\text{ g Cd(OH)}_2 \times \dfrac{1\text{ mol Cd(OH)}_2}{146.4\text{ g Cd(OH)}_2} \times \dfrac{2\text{ mol } e^-}{1\text{ mol Cd}} \times \dfrac{9.648 \times 10^4\text{ C}}{1\text{ mol } e^-} = 170.0\text{ C}$

$170.0\text{ C} \times \dfrac{1\text{ A} \cdot \text{s}}{1\text{ C}} \times \dfrac{1}{0.175\text{ A}} = 971\text{ s} = 0.270\text{ h}$

83. $\text{mol M} = 0.600\text{ A} \times 1\text{ h} \times \dfrac{3600\text{ s}}{1\text{ h}} \times \dfrac{1\text{ C}}{1\text{ A} \cdot \text{s}} \times \dfrac{1\text{ mol } e^-}{9.648 \times 10^4\text{ C}} \times \dfrac{1\text{ mol M}}{1\text{ mol } e^-} = 0.0224$

MM of M = 2.42 g/0.0244 mol = 108 g/mol

85. $\text{Zn(OH)}_4^{2-}(aq) + 2e^- \rightarrow \text{Zn}(s) + 4\text{OH}^-(aq) \qquad E^\circ_{\text{red}} = -1.19\text{ V}$

$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^- \qquad E^\circ_{\text{ox}} = +0.76\text{ V}$

$\text{Zn(OH)}_4^{2-}(aq) \rightarrow \text{Zn}^{2+}(aq) + 4\text{OH}^-(aq) \qquad E^\circ = -0.43\text{ V}$

$\text{Zn}^{2+}(aq) + 4\text{OH}^-(aq) \rightarrow \text{Zn(OH)}_4^{2-}(aq) \qquad E^\circ = +0.43\text{ V}$

$\ln K = \dfrac{nE^\circ}{0.0257\text{ V}} = \dfrac{(2)(0.43\text{ V})}{0.0257\text{ V}}; \quad K = 3 \times 10^{14}$

87. (d)

89. $\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s) \qquad E^\circ_{\text{red}} = 0.799\text{ V}$

$\text{Ag}(s) + \text{SCN}^-(aq) \rightarrow \text{AgSCN}(s) + e^- \qquad E^\circ_{\text{ox}} = -0.0895\text{ V}$

$\text{Ag}^+(aq) + \text{SCN}^-(aq) \rightarrow \text{AgSCN}(s) \qquad E^\circ = 0.709\text{ V}$

$\ln \dfrac{1}{K_{\text{sp}}} = \dfrac{(1)(0.709\text{ V})}{0.0257\text{ V}}; \quad K = 1 \times 10^{-12}$

91. (a) EQ (b) LT (c) GT (d) EQ (e) MI

93. Assume 10.00 A for 10.00 min (600.0 s) as total current.

For Sn, current supplied = $(10.00\text{ A})(600.0\text{ s})(0.200) = 1.20 \times 10^3\text{ A} \cdot \text{s} = 1.20 \times 10^3\text{ C}$

$\text{mass Sn} = 1.20 \times 10^3\text{ C} \times \dfrac{1\text{ mol } e^-}{9.648 \times 10^4\text{ C}} \times \dfrac{1\text{ mol Sn}^{2+}}{2\text{ mol } e^-} \times \dfrac{118.69\text{ g Sn}}{1\text{ mol Sn}^{2+}} = 0.738\text{ g}$

For Cu, current supplied = $(10.00\text{ A})(600.0\text{ s})(0.800) = 4.80 \times 10^3\text{ A} \cdot \text{s} = 4.80 \times 10^3\text{ C}$

$\text{mass Cu} = 4.8 \times 10^3\text{ C} \times \dfrac{1\text{ mol } e^-}{9.648 \times 10^4\text{ C}} \times \dfrac{1\text{ mol Cu}^{2+}}{2\text{ mol } e^-} \times \dfrac{63.55\text{ g Cu}}{1\text{ mol Cu}^{2+}} = 1.58\text{ g}$

Total mass = (1.58 + 0.738) g = 2.32 g

$\%\text{ Sn} = \dfrac{0.738\text{ g}}{2.32\text{ g}} \times 100\% = 31.8\%; \quad \%\text{ Cu} = 100 - 31.8 = 68.2\%$

94. $Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O$

$\Delta G^\circ = -371.4$ kJ (see page 502) ; $\quad E^\circ = -\dfrac{3.741 \times 10^5 \text{ J/mol}}{(2)(9.648 \times 10^4 \text{ J/mol} \cdot \text{V})} = 1.925$ V

Consider 1000.0 g of solution: mol $H_2SO_4 = 380 \text{ g} \times \dfrac{1 \text{ mol}}{98.08 \text{ g}} = 3.87$

$V = 1000.0 \text{ g} \times \dfrac{1 \text{ cm}^3}{1.286 \text{ g}} \times \dfrac{1 \text{ L}}{1000 \text{ cm}^3} = 0.778$ L; $\quad [H_2SO_4] = \dfrac{3.87 \text{ mol}}{0.778 \text{ L}} = 4.98\ M = [H^+] = [HSO_4^-]$

$E = 1.925 \text{ V} - \dfrac{0.0257 \text{ V}}{2} \ln \dfrac{1}{(4.98)^4} = 2.007$ V

95. (a) $E^\circ = 0.621$ V

(b) $[Zn^{2+}]$ increases, $[Sn^{2+}]$ decreases

(c) $0 = 0.621 \text{ V} - \dfrac{0.0257 \text{ V}}{2} \ln Q$; $\quad Q = 1 \times 10^{21}$

(d) $[Zn^{2+}] = 2.0\ M$; $\quad [Sn^{2+}] = 2 \times 10^{-21}\ M$

96. (a) $\Delta G^\circ = -(2)(9.648 \times 10^4 \text{ J/mol} \cdot \text{V})(-0.581 \text{ V}) = 1.12 \times 10^5$ J

$\Delta G^\circ = -(2)(9.648 \times 10^4 \text{ J/mol} \cdot \text{V})(-0.197 \text{ V}) = 0.38 \times 10^5$ J

$\Delta G^\circ_{tot} = 1.50 \times 10^5$ J

(b) $E^{\circ\prime} = -\dfrac{1.50 \times 10^5 \text{ J}}{(4)(9.648 \times 10^4 \text{ J/mol} \cdot \text{V})} = -0.389$ V

97. anode: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$ $\quad E_{ox} = 0.00 \text{ V} - \dfrac{0.0257 \text{ V}}{2} \ln (1 \times 10^{-7})^2 = +0.414$ V

cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$ $\quad E_{red} = 0$ V

$E = +0.414$ V

98. mol $H_2 = \dfrac{(1.0 \text{ L})(200 \text{ atm})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298 \text{ K})} = 8.17$

$8.17 \text{ mol } H_2 \times \dfrac{2 \text{ mol } e^-}{1 \text{ mol } H_2} \times \dfrac{9.648 \times 10^4 \text{ C}}{1 \text{ mol } e^-} \times \dfrac{1 \text{ A} \cdot \text{s}}{1 \text{ C}} \times \dfrac{1}{1.5 \text{ A}} = 1.05 \times 10^6 \text{ s} = 12$ days